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**Acetic Acid Recovery Method**

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**(54) [Title of the Invention]**

**Acetic Acid Recovery Method**

**(57) [Summary]**

**[Object]** To provide an extremely economical, industrially beneficial method whereby acetic acid can be recovered efficiently and at low cost from an aqueous solution containing acetic acid and methyl acetate that is obtained by means of a process in which an alkyl aromatic hydrocarbon is oxidized in the liquid phase in a lower aliphatic carboxylic acid (specifically, acetic acid) in the presence of a heavy metal-containing catalyst with the help of a gas that

contains molecular oxygen, and in which distillation is performed to separate the component of the mixture of water, methyl acetate, and acetic acid generated as a result of the oxidation.

**[Means of Achievement]** A method of recovering acetic acid from an aqueous solution containing acetic acid and methyl acetate, wherein the acetic acid recovery method is characterized in comprising steps (1) through (4) below:

(1) an extraction step for separating acetic acid-containing water that contains acetic acid and methyl acetate into an extract phase comprising a water-containing extraction residue and an extracting agent that contains acetic acid as a result of performing extraction using an extracting agent with a lower boiling point than acetic acid;

(2) a distillation step for distilling and separating the extract phase and separating the acetic acid and extracting agent;

(3) a methyl acetate recovery step for separating and recovering methyl acetate from the separated extracting agent; and

(4) a step for recycling the extracting agent from which acetic acid and methyl acetate have been separated.

**[Claims]**

**[Claim 1]** A method of recovering acetic acid from an aqueous solution containing acetic acid and methyl acetate, said acetic acid recovery method characterized in comprising steps (1) through (4) below:

(1) an extraction step for separating acetic acid-containing water that contains acetic acid and methyl acetate into an extract phase comprising a water-containing extraction residue and an extracting agent that contains acetic acid as a result of performing extraction using an extracting agent with a lower boiling point than acetic acid;

(2) a distillation step for distillation separating the extract phase and separating the acetic acid and extracting agent;

(3) a methyl acetate recovery step for separating and recovering methyl acetate from the separated extracting agent; and

(4) a step for recycling the extracting agent from which acetic acid and methyl acetate have been separated.

**[Claim 2]** The acetic acid recovery method according to claim 1, wherein the aqueous solution containing acetic acid and methyl acetate is a distillate containing water and methyl acetate obtained by means of distilling acetic acid.

**[Claim 3]** The acetic acid recovery method according to claim 1 or 2, wherein the aqueous solution containing acetic acid and methyl acetate is a byproduct from an alkyl aromatic oxidation step.

**[Claim 4]** The acetic acid recovery method according to claim 3, wherein the recovered methyl acetate is recycled into the alkyl aromatic oxidation step.

**[Claim 5]** The acetic acid recovery method according to any of claims 1 through 4, wherein the removal of methyl acetate from the extracting agent in step (3) is performed by means of distillation.

**[Claim 6]** The acetic acid recovery method according to any of claims 1 through 5, wherein the extraction residue separated in step (1) is separated into water and extraction agent by means of a distillation separation.

**[Claim 7]** The acetic acid recovery method according to any of claims 1 through 6, wherein the extracting agent that remains from the recovery of methyl acetate in step (3) is recycled into the extraction in step (1).

**[Claim 8]** The acetic acid recovery method according to claim 6 or 7, wherein methyl acetate is recovered from the extracting agent separated and recovered from the extraction residue, and the remainder thereof is reused in extraction.

#### **[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to a method of recovering acetic acid from an aqueous solution that contains acetic acid and methyl acetate. More specifically, the present invention relates to a method whereby acetic acid can be recovered efficiently from an aqueous solution containing acetic acid and methyl acetate that is obtained by means of a process in which an alkyl aromatic hydrocarbon is oxidized in the liquid phase in a lower aliphatic carboxylic acid (specifically, acetic acid) in the presence of a heavy metal-containing catalyst with the help of a gas that contains molecular oxygen, and water is separated

by means of a distillation from the mixture of methyl acetate and acetic acid generated as a result of the oxidation.

**[0002]**

**[Prior Art]** Distillation recovery is one example of a known conventional method of acetic acid recovery. This distillation recovery method is disclosed in Netherlands Patent No. 73-16510, Federal Republic of Germany Patent No. 3408239, Soviet Union Patent No. 1268564, and JP (Kokai) No. H6-65139, but when the acetic acid concentration of the distillate at the top of the distillation column for acetic acid is low at about 1 % by weight, a large number of theoretical plates and a high reflux ratio become necessary due to the highly non-ideal properties of an acetic acid/water system and the equilibrium limit in such an apparatus, and more efficient acetic acid recovery becomes difficult in terms of equipment, energy, and other aspects. The wastewater from this process is currently decomposed with the help of an activated sludge method, direct incineration method, or the like, which is undesirable in terms of the environment and effective use of resources.

**[0003]** Other examples include methods of recovery by means of an esterification, and examples thereof are proposed in Netherlands Patent No. 40969 and JP (Kokai) No. S59-29633. However, these methods require both esterification and hydrolysis steps, which necessitate alcohol removal, water removal, and other separation operations, thereby lengthening the entire process and increasing equipment costs.

**[0004]** Another example is extraction with the help of an organic solvent. Methods using phosphane oxide (JP (Kokai) No. S63-44539), an amine and phosphoric acid ester (JP (Kokai) No. S55-154935), phosphoric acid ester (JP (Kokai) No. S57-56002), or other organic solvent are proposed. More acetic acid is apparently recovered as a result of these methods than by means of previous methods.

**[0005]** A method is also proposed whereby acetic acid is recovered using methyl acetate as an extracting agent generated as a byproduct from the reaction system in the process of manufacturing terephthalic acid (JP (Kokai) No. S63-156744), but since the extracting agent methyl acetate has high solubility in water, a homogenous phase is formed when the acetic acid concentration in the acetic acid-water-methyl acetate solution reaches at least approximately 5%

or above, and such an extracting agent is therefore not considered to be suitable for acetic acid recovery by means of an extraction.

[0006] Furthermore, acetic acid recovery as a result of extraction in a terephthalic acid manufacturing process or the like is proposed in JP (Kokai) No. H7-53443. However, methyl acetate is included in the acetic acid-containing water formed as a byproduct from manufacturing plants that use oxidation of terephthalic acid or another alkyl aromatic hydrocarbons, and it is difficult to selectively extract only acetic acid with the help of any of the above-mentioned methods. Also, when an extracting agent with a lower boiling point than acetic acid is used in the conventional methods, almost all of the methyl acetate in the acetic acid-containing water accumulates in high concentration in the extracting agent, and part of it is discharged along with the wastewater, so effective extraction recovery of acetic acid becomes impossible.

[0007] Methods are also proposed whereby acetic acid recovery by means of an extraction is performed after decomposing an organic substance other than acetic acid with a catalyst, such as in JP (Tokugan) No. H9-122663. This method is, in fact, considered to be capable of recovering acetic acid with few impurities. On the other hand, however, while such a method prevents the loss of acetic acid as a result of returning byproduct methyl acetate to the reaction system in a terephthalic acid manufacturing plant, the methyl acetate that is the active ingredient for preventing loss of acetic acid may decompose in this method, which is undesirable from the perspective of recycling useful resources.

[0008]

**[Problems to Be Solved by the Invention]** Therefore, as a result of concentrated investigation of a method for treating acetic acid-containing water, the inventors discovered that a method whereby acetic acid separation treatment by means of an extraction is performed on an aqueous solution containing acetic acid and methyl acetate, acetic acid is recovered from the extracting agent phase, and the active ingredient methyl acetate is separated, recovered, and recycled into the reaction system is extremely effective at recovering acetic acid generated as a byproduct from the oxidation of an alkyl aromatic, and thus developed the present invention.



**[0009]**

**[Means Used to Solve the Above-Mentioned Problems]** The present invention is a method for recovering acetic acid from an aqueous solution containing acetic acid and methyl acetate, and essentially consists of an acetic acid recovery method that is characterized in having steps (1) through (4) below:

**[0010]** (1) an extraction step for separating acetic acid-containing water that contains acetic acid and methyl acetate into an extract phase comprising a water-containing extraction residue and an extracting agent that contains acetic acid as a result of performing an extraction using an extracting agent with a lower boiling point than acetic acid;

(2) a distillation step for distillation separating the extract phase and separating the acetic acid and extracting agent;

(3) a methyl acetate recovery step for separating and recovering methyl acetate from the separated extracting agent; and

(4) a step for recycling the extracting agent from which acetic acid and methyl acetate have been separated.

**[0011]**

**[Embodiments of the Invention]** The present invention will be described in detail hereinafter.

The acetic acid recovery method of the present invention can be applied mainly to an aqueous solution generated as a byproduct from an oxidation reaction process in a chemical factory.

Specifically, this method is preferably used in the recovery of acetic acid from a mixture of water, acetic acid, and methyl acetate generated when an alkyl aromatic hydrocarbon is oxidized in the liquid phase in a lower aliphatic carboxylic acid (acetic acid, for example) with the help of a molecular oxygen-containing gas in the presence of a catalyst containing a heavy metal.

**[0012]** Specifically, in the present invention, an aqueous solution is preferably used that contains acetic acid and methyl acetate and is obtained as a distillate from distilling acetic acid that contains water and methyl acetate recovered from a process for manufacturing terephthalic acid as a result of the liquid-phase oxidation of an alkyl aromatic hydrocarbon such as paraxylene, for example, in acetic acid as a solvent with the help of a molecular oxygen-containing gas in the presence of a catalyst that contains a heavy metal. The concentrations of components in the aqueous solution are not particularly limited, but the acetic acid concentration is usually 1 % by

weight or above, preferably 5 % by weight or above, and particularly preferably 10 % by weight or above with respect to the aqueous solution. The acetic acid concentration is preferably not too low, because the reboiler load increases in the distillation column for distilling acetic acid that contains water and methyl acetate. On the other hand, the maximum acetic acid concentration is usually 50 % by weight or less, preferably 40 % by weight or less, and more preferably 30 % by weight or less. The acetic acid concentration is preferably not too high, because the load increases on the extracting apparatus used in step (2) above.

**[0013]** Acetic acid recovery is performed in the above-mentioned steps (1) and (2) in the present invention. Extraction is employed in the recovery operation. An extracting agent and extraction apparatus must be selected for the extraction step. The extracting agent for performing the acetic acid extraction must have a lower boiling point than that of acetic acid. Furthermore, a solvent is used which has a large partition coefficient with respect to acetic acid. Specific examples include methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl isobutyl ketone, and other ketones; butanol and other alcohols; and ethyl acetate, propyl acetate, and other esters. One or more types of the above-mentioned solvents are used. A solvent is preferably used whose boiling point is at least 20°C apart from those of acetic acid and the extracting agent in order to effectively separate acetic acid from the extracting agent after the acetic acid extraction. The extraction column may be of the usual type, and suitable examples thereof include a mixer settler extraction column, porous plate, packed column, baffle column, vibrating porous plate, stirring and mixing apparatus, pulse filling apparatus, or other type. The extract phase having the extracting agent obtained as a result of this extraction as the main component thereof is aftertreated by means of distillation. If the difference in boiling point between acetic acid and the extracting agent is large enough, high-purity acetic acid can be easily recovered by means of an ordinary distillation.

**[0014]** In the present invention, after the acetic acid in the aqueous solution containing acetic acid and methyl acetate is recovered as a result of the above-mentioned method or other method, removal/recovery of methyl acetate from the remaining extracting agent is then performed in the above-mentioned step (3). The removal/recovery is preferably performed by means of a distillation treatment. A distillation apparatus must be selected for the distillation operation. A tray column, packed column, or the like, for example, may be used as the distillation column. Suitable types of trays or filling materials include, for example, sieve tray and mini-valve types,



and regular or non-regular filling materials. Methods for separating and recovering methyl acetate in a distillation column at normal pressure with the column top at 64°C and the column bottom at 71°C, for example, are included in this distillation operation.

[0015] In the case of a manufacturing process for obtaining terephthalic acid as a result of oxidizing paraxylene in an acetic acid solvent with the help of a molecular oxygen-containing gas in the presence of a catalyst that contains a heavy metal, it is known that the concentration of methyl acetate in the reaction vessel can be increased and the loss due to formation of methyl acetate as a byproduct from the acetic acid used as a solvent can be greatly reduced as a result of recycling the recovered methyl acetate into the oxidation reaction system (JP (Kokoku) No. S56-45899). The unit consumption of acetic acid is thereby reduced, which is a significant industrial advantage.

[0016] All or part of the extracting agent recovered from the above-mentioned step is preferably recycled into the extraction step. Also, the extracting agent supplied to the extraction step is preferably replenished in the amount needed for the extraction step. An embodiment of the present invention will next be described with reference to the figure. Fig. 1 depicts a schematic example of the method of the present invention.

[0017] Firstly, acetic acid containing water and methyl acetate transported via line 1 from a manufacturing plant for terephthalic acid or the like is separated into an acetic acid component by the acetic acid dehydrating column 2 from the column bottom line 3, and an aqueous solution that contains acetic acid and methyl acetate from the column top line 4. The acetic acid-containing water taken from line 4 is cooled with the help of a heat exchanger 8 and fed to the distillation column 10. The extracting agent is fed to the extraction column 10 via the line 9. Both products are brought into contact in a countercurrent inside the extraction column 10, and acetic acid is extracted in an extract phase that contains the extracting agent. The extract phase (line 12) taken from the top of the extraction column 10 is sent to the acetic acid recovery column 14. Also, the extraction residue (line 11) taken from the bottom of the extraction column 10 is sent to the solvent recovery column 22. The extract phase is separated as a result of distillation in the acetic acid recovery column 14 into an acetic acid component and a water-containing extracting agent component. The acetic acid component is taken from the bottom of the column (line 15) and recycled for use in the system as recovered acetic acid. On the other hand, the extraction residue is separated as a result of distillation in the extracting agent recovery

column 22 into a water-containing extracting agent component (line 24) and treated water (line 23). The treated water is taken from the bottom of the extracting agent recovery column 22 and purged from the system. The water-containing extracting agent components, taken from the top of the acetic acid recovery column 14 and the top of the extracting agent recovery column 22, are cooled with the help of the heat exchangers 17 and 25, fed together to the liquid-liquid separator 18, and separated into a component that mainly consists of recovered extracting agent (upper layer) and a component that mainly consists of water (lower layer). The component primarily consisting of water is sent to the extracting agent recovery column 22 as reflux solution (line 20), and is reintroduced to the distillation separation of the extraction residue. The component primarily consisting of water is ultimately purged (line 23) as treated water from the bottom of the extracting agent recovery column 22. Also, the component primarily consisting of recovered extracting agent is sent to the acetic acid recovery column 14 and the methyl acetate recovery column 5 via line 19, and is separated into a recovered extracting agent from line 6 at the bottom of the methyl acetate recovery column 5 and a methyl acetate component from line 7 at the top of the column. This methyl acetate component is recycled into the oxidation reaction system for terephthalic acid or the like. The recovered extracting agent taken from line 6 is circulated to the extraction column 10 and reused. Also, the lost portion of the extracting agent is replenished from line 27.

[0018]

**[Working Examples]** The present invention will be described in further detail with the help of the working examples described hereinafter, but the present invention is not limited by these examples inasmuch as they do not exceed the scope of the present invention. Also, "parts" in the working examples refers to "weight parts."

**[0019] Working Example 1**

Paraxylene was continuously oxidized in a titanium reactor at a reaction temperature of 210°C, a reaction pressure of 25 kg/cm<sup>2</sup>, and a residence time of 120 minutes using as a solvent aqueous acetic acid containing 300 ppm of cobalt acetate (as Co atoms), 200 ppm of manganese acetate (as Mn atoms), and 1000 ppm of hydrobromic acid (as Br atoms) with respect to the solvent. The following products were obtained: a solution obtained as a result of the partial removal of a reflux condensable component obtained by means of condensing waste gas from the

oxidation reaction; an absorption solution in which components in the oxidation waste gas are absorbed into water, and distilled vapor obtained as a result of the removal of catalyst components, intermediate reaction products, and reaction byproducts in a solvent flushing distillation column from part of the reaction mother liquid obtained by means of a solid-liquid separation. All these products consisted of acetic acid that contained water and methyl acetate, and they were introduced into an acetic acid dehydration column with 70 stages, a temperature of 100°C at the top of the column, and a temperature of 120°C at the bottom of the column. Acetic acid containing 7.2 % by weight of water was recovered from the bottom of the column, and an aqueous solution primarily consisting of water (acetic acid: 15.3 % by weight; methyl acetate: 2.6 % by weight) was obtained at a rate of 20.4 parts/hr from the top of the column.

[0020] The aqueous solution was then cooled and continuously fed to an RDC-type extraction column (stages: 55) from the column top. The extracting agent ethyl acetate was also continuously fed from the bottom of the extraction column. The extracting agent/aqueous solution ratio (weight ratio) at this time was equal to 2. An extraction residue primarily consisting of water and containing ethyl acetate according to the solubility thereof was obtained from the bottom of the extraction column, and an extract phase primarily consisting of the extracting agent ethyl acetate from which acetic acid had been extracted was obtained from the top of the extraction column. The extraction residue primarily consisting of water obtained from the bottom of the extraction column was introduced into a 10-stage extracting agent recovery column with a temperature of 71°C at the top of the column and 100°C at the bottom of the column, and 15.0 parts/hr of treated water (acetic acid: 550 ppm) were obtained from the bottom of the column. Also, the extract phase primarily consisting of extracting agent obtained from the top of the extraction column was introduced into a 24-stage acetic acid recovery column with a temperature of 71°C at the top of the column and 103°C at the bottom of the column, and 4.8 parts/hr of recovered acetic acid (acetic acid: 64.8 % by weight) were recovered from the bottom of the column. The extracting agent components that contained water and were taken from the top of the acetic acid recovery column and the top of the extracting agent recovery column were cooled with the help of heat exchangers, fed together to the liquid-liquid separator, and separated into a component primarily consisting of recovered extracting agent and a component primarily consisting of water. The component primarily consisting of water was sent to the extracting agent recovery column as a reflux solution and submitted for distillation

separation. This water component was purged as treated water from the bottom of the extracting agent recovery column. The component primarily consisting of recovered extracting agent was also introduced into a 20-stage methyl acetate recovery column with a temperature of 64°C at the top of the column, a temperature of 71°C at the bottom of the column, and a reflux ratio of 50; 0.6 parts/hour of a solution primarily consisting of methyl acetate was recovered from the top of the column; and recovered extracting agent was obtained from the bottom of the column. The solution consisting mainly of recovered methyl acetate was recycled into the reaction system. Also, the recovered extracting agent was circulated and reused in the extraction column.

#### **[0021]**

**[Effect of the Invention]** As described above, the method of the present invention allows acetic acid to be recovered more efficiently and with minimal loss compared to current distillation methods, and provides an extremely economical and industrially advantageous method.

#### **[Brief Description of the Drawings]**

**[Figure 1]** Fig. 1 is a schematic view depicting an example of the process of the present invention.

#### **[Key]**

- 1, 3, 4, 6, 7, 9, 11, 12, 15, 16, 19, 20, 21, 23, 24, 26, and 27: piping
- 8, 13, 17, 25, and 28: heat exchangers
- 2: acetic acid dehydration column
- 5: methyl acetate recovery column
- 10: extraction column
- 14: acetic acid recovery column
- 18: liquid-liquid separator
- 22: extracting agent recovery column

The diagram illustrates a chemical process involving distillation and heat exchange. The main components and their connections are as follows:

- Distillation Column 2:** Receives feed stream 1. Its top product is stream 4, which passes through a condenser (circular symbol with a zigzag line) and a reboiler (circular symbol with a zigzag line) before entering Distillation Column 10. Its bottom product is stream 3, which passes through a reboiler.
- Distillation Column 10:** Receives stream 4 from Column 2 and stream 8 from a reboiler. Its top product is stream 12, which goes to Distillation Column 24. Its bottom product is stream 11, which goes to Distillation Column 22.
- Distillation Column 24:** Receives stream 12. Its top product is stream 25, which goes to a condenser. Its bottom product is stream 23, which goes to a reboiler.
- Distillation Column 22:** Receives stream 11. Its top product is stream 20, which goes to a condenser. Its bottom product is stream 23, which goes to a reboiler.
- Distillation Column 18:** Receives stream 20 from Column 22 and stream 17 from a condenser. Its top product is stream 16, which goes to Distillation Column 14. Its bottom product is stream 21, which goes to Distillation Column 14.
- Distillation Column 14:** Receives stream 16 and stream 21 from Column 18. Its top product is stream 15, which goes to a condenser. Its bottom product is stream 26, which goes to Distillation Column 5.
- Distillation Column 5:** Receives stream 26. Its top product is stream 7, which goes to a condenser. Its bottom product is stream 6, which goes to a reboiler.
- Heat Exchangers:** There are several heat exchangers represented by circular symbols with zigzag lines. Stream 8 is heated by stream 11 in a reboiler. Stream 28 is heated by stream 11 in a reboiler. Stream 27 is heated by stream 11 in a reboiler. Stream 25 is cooled by stream 20 in a condenser. Stream 17 is cooled by stream 20 in a condenser. Stream 15 is cooled by stream 21 in a condenser. Stream 7 is cooled by stream 6 in a condenser.

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